

## Early failure of high-power white LEDs for outdoor applications under extreme electrical stress: Role of silicone encapsulant

A. Caria<sup>a,\*</sup>, R. Fraccaroli<sup>a</sup>, G. Pierobon<sup>a</sup>, T. Castellaro<sup>a</sup>, G. Mura<sup>b</sup>, P.C. Ricci<sup>c</sup>, C. De Santi<sup>a</sup>, M. Buffolo<sup>a</sup>, N. Trivellin<sup>d</sup>, E. Zanoni<sup>a</sup>, G. Meneghesso<sup>a</sup>, M. Meneghini<sup>a,e</sup>

<sup>a</sup> Department of Information Engineering, University of Padova, via Gradenigo 6/B, Padova 35131, Italy

<sup>b</sup> Department of Electrical and Electronic Engineering, University of Cagliari, Piazza D'Armi, Cagliari 09123, Italy

<sup>c</sup> Department of Physics, University of Cagliari, Cittadella Universitaria, S.P. n° 8 km 0,700, Monserrato, CA 09042, Italy

<sup>d</sup> Department of Industrial Engineering, University of Padova, Via Marzolo 9, Padova 35131, Italy

<sup>e</sup> Department of Physics and Astronomy, University of Padova, via Marzolo 8, Padova, 35131 Padova, Italy

### ARTICLE INFO

#### Keywords:

Light emitting diodes  
Solid state lighting  
Robustness  
Silicone degradation  
Raman

### ABSTRACT

Solid state lighting systems have deeply penetrated the market and are widely available. White light emitting diodes (LEDs) are based on a gallium nitride blue-emitting chip and a phosphor-based layer is used to convert blue radiation to white light, in combination with an optical system to enhance light extraction. High temperatures can be detrimental for LED reliability, resulting in a gradual or catastrophic failure. Therefore, the design of such devices, especially in relation to use cases that require operation at high current and temperature levels, needs to be based on reliability considerations.

In this work we analyze the robustness of high power white LEDs submitted to driving currents exceeding the nominal levels by means of electrical and optical characterization, as well as on failure analysis techniques. The results highlight a significant degradation of the main optical parameters (luminous flux, color coordinates, correlated color temperature, ...). Device cross sectioning highlighted a heavy darkening of the silicone material in the overstressed devices, and a delamination of the phosphors. Raman spectroscopy analysis highlighted an enhancement in luminescence of degraded samples. Such degradation was ascribed to the high temperature reached by the LEDs during the stress, that caused the degradation of the silicone lens; the process can be enhanced by the low efficiency of the phosphors and LEDs at high temperatures, resulting in a stronger heating of the devices.

### 1. Introduction

Solid state lighting systems are nowadays widely diffused and have deeply penetrated the market, thanks to their cost effectiveness, efficiency and reliability [1]. Light-emitting diodes (LEDs) based on GaN allow to develop novel and innovative approaches to lighting, meeting the needs of several use cases, from indoor to outdoor illumination, from automotive to horticulture. The reliability of SSL systems heavily depends on the conditions in which the system runs, in particular the temperature and the luminous flux [2–5]. In many scenarios, such as outdoor lighting and automotive applications, small and high intensity light sources are needed. For this reason, LEDs are often used close to their current/temperature limits. Human-centric lighting requires light sources that are reliable both in terms of flux output and color stability,

since can heavily influence human activities [6]. Therefore, a study of LED reliability and robustness in harsh conditions (close to or beyond the absolute maximum ratings) is necessary to evaluate the related ageing indicators and degradation processes.

In this work, we present the results of a degradation stress test performed on white high-power LEDs for outdoor lighting. We performed the stress at high ambient temperature and at currents ranging from the absolute maximum rating to 1.6 times this value. Devices stressed in such conditions operate at very high temperatures, that can be detrimental for the device integrity. In real life operation, such high temperatures could be reached even when operating the device within the current ratings, due to bad thermal management, or due to the ageing of the luminaire, due to degradation of thermal interface materials, failure of heat dissipation systems and unfavorable operating environments

\* Corresponding author.

E-mail address: [alessandro.caria@unipd.it](mailto:alessandro.caria@unipd.it) (A. Caria).

<https://doi.org/10.1016/j.microrel.2023.115142>

Received 5 June 2023; Received in revised form 3 July 2023; Accepted 19 July 2023

Available online 1 October 2023

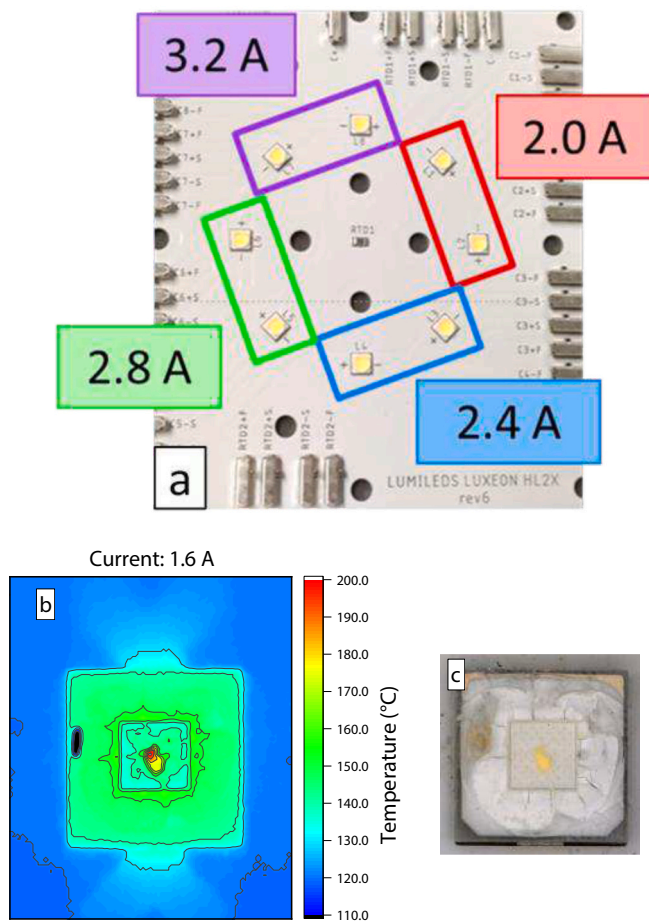
0026-2714/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

(especially ambient temperature). The results highlighted a heavy degradation of the optical components of the device when exceeding manufacturer specifications. Device electro-optical characterization was used to identify the main changes of the electro-optical characteristics; in addition, cross sectioning was carried out, to identify the origin of degradation. Photoluminescence and Raman spectroscopy analysis were carried out on the lens to better understand the role of the optical system in degradation.

## 2. Experimental details

The devices under analysis are commercially available LEDs, with a nominal correlated color temperature of 4000 K, a nominal color rendering index of 70, 3535 ceramic package and a die size of  $2 \text{ mm}^2$ . These LEDs feature an absolute maximum current rating of 2.5 A at junction temperature  $T_j = 125 \text{ }^\circ\text{C}$ , and of 2.0 A at  $T_j = 135 \text{ }^\circ\text{C}$ . Devices have an ESD protection diode, connected in parallel with the LED, with a turn on voltage lower than  $-8 \text{ V}$ . The devices were mounted on custom metal-core printed circuit board (MCPCB), featuring two Pt100 resistive thermal devices to sense PCB temperature, one of the center and one on the side of the PCB. The MCPCB have 8 LEDs (named L1, L2, ... L8), with a pitch around 10 mm between them, connected in series, each one featuring a 4 wire connection for accurate electrical characterization. The PCB was mounted on an  $112 \times 112 \times 72 \text{ mm}$  aluminum heat sink, dimensioned to handle several tens of watt of power dissipation, with a Kerafol Keratherm Red high conductivity ( $6.5 \text{ W/m}\cdot\text{K}$ ) thermal interface to enhance thermal coupling.

Devices were characterized by means of electrical and optical



**Fig. 1.** (a) metal core printed circuit board with the 8 LEDs; the stress currents for each two-LED series are indicated. (b) thermal image of a device stressed at 1.6 A and (c) optical image of the same device.

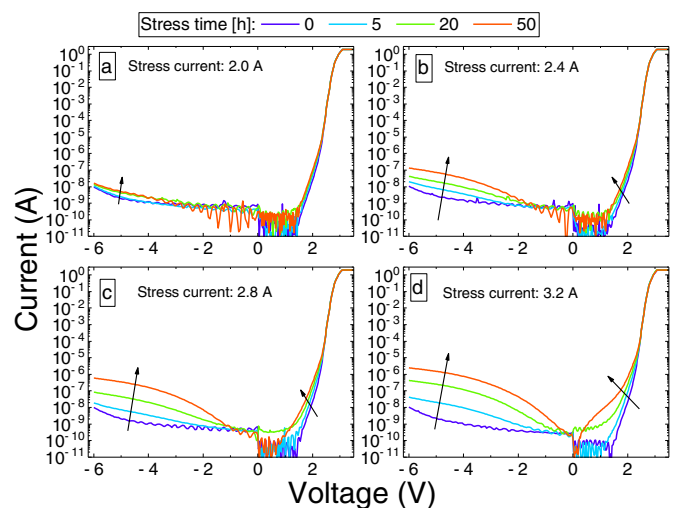
measurements. Electrical characterization was carried out by a semiconductor parameter analyzer, that allowed sweep I-V characterization and served as current source for power spectral density (PSD) measurements. Absolute irradiance characterization was made by a Labsphere LMS-650 65" integrating sphere, calibrated by a NIST traceable calibration source. Each LED was measured individually. Stress was performed by connecting the LEDs two by two in series, allowing to have 4 pairs of LEDs stressed at 2.0 A (L1 and L2), 2.4 A (L3 and L4), 2.8 A (L5 and L6) and 3.2 A (L7 and L8), corresponding 1, 1.2, 1.4 and 1.6 times the absolute maximum rating at  $T_j = 125 \text{ }^\circ\text{C}$ , respectively. Ambient temperature was set at  $T_{\text{oven}} = 85 \text{ }^\circ\text{C}$ . MCPCB picture is shown in Fig. 1 (a), along with the stress currents of each two-LED series. During stress, the center of the PCB reached  $\sim 120 \text{ }^\circ\text{C}$ . The junction temperatures of the LEDs were estimated by the forward bias method [7]: L1 and L2 reached  $180 \text{ }^\circ\text{C}$ , whereas other LEDs stressed at higher currents exceed  $200 \text{ }^\circ\text{C}$ . A further analysis was performed by means of thermal imaging on an additional LED with lens removed and stressed at 1.6 A, shown in Fig. 1 (b-c). This LED has some residuals of phosphors on its surface, and temperatures measured are around  $150 \text{ }^\circ\text{C}$  on the bare chip surface and exceed  $200 \text{ }^\circ\text{C}$  on the region with phosphors residuals.

## 3. Analysis of degradation

For each stress condition, the devices were stressed for a total of 50 h, until the devices failed. The I-V curves were measured at each step of the stress by a fast sweep measurement in the range between  $-6 \text{ V}$  (to avoid the protection diode turn-on) and  $3.5 \text{ V}$ , with a 2 A current compliance (the plateau of the I-V curve).

The results are reported in Fig. 2 for 4 of the 8 LEDs, one for each stress current. The noise floor of the measurements was around  $10^{-10} \text{ A}$  and is visible in the region between 0 and 1.5 V. The results show a gradual increase in both reverse and forward leakage current, that is enhanced by higher stress conditions. The variation in leakage is related to an enhancement of trap-assisted tunneling and/or variable range hopping mechanisms, due to an increase in defects density [8–10], that is accelerated by a higher stress current levels. Absolute spectral measurements were performed from low currents (0.05 A) to the absolute maximum rating. From PSDs, optical power and colorimetric properties of the LEDs were calculated. Fig. 3 reports the optical power normalized to the value measured on the unstressed device and the variation of the CIE1931 xy color coordinates during the stress for the LEDs under analysis.

The optical power of the LED stressed at the absolute maximum current (i.e. 2 A) shows almost no degradation, as its variation is below



**Fig. 2.** I-V characterizations of LED stressed at 2.0 A (a), 2.4 A (b), 2.8 A (c) and 3.2 A (d).

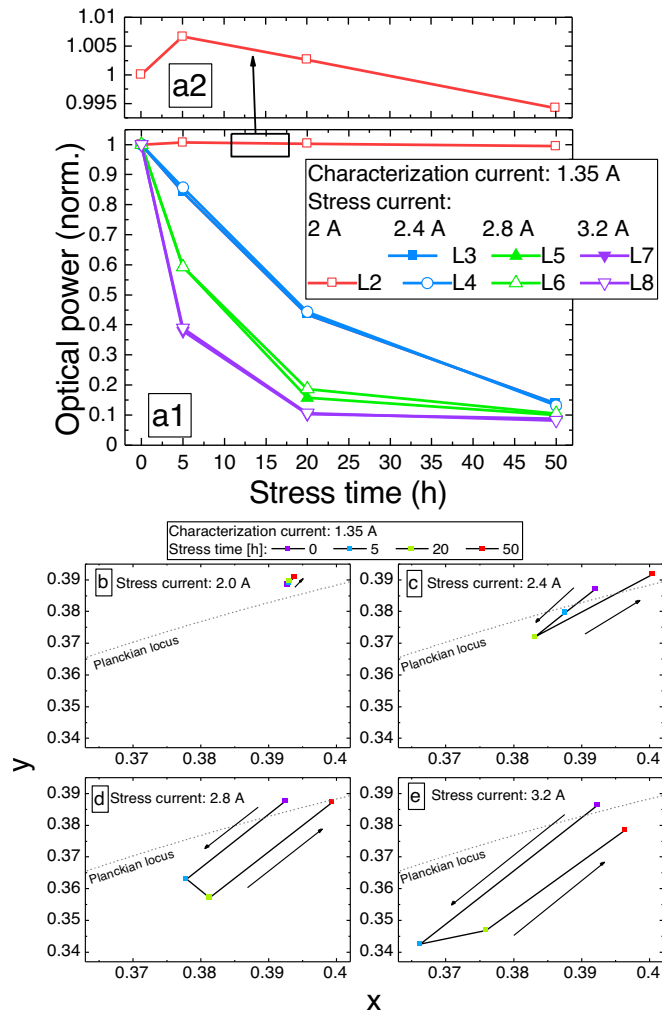


Fig. 3. Optical power normalized with respect to the unstressed sample (a1) with details of L1 stressed at 2.0 A (a2) and variation of the xy CIE1931 color coordinates (b-e) calculated from the measured PSDs for the various LEDs under stress. All the measurements were made at 1.35 A.

1 %, that is close to the accuracy limit of the system used for the optical measurements. The LEDs stressed above this current threshold show a substantial decrease in their optical power, reaching a level that is below 20 % of the initial optical power after 50 h of stress. LEDs stressed at higher currents exhibit a faster degradation, losing the 60 % of their optical power during the first 5 h of stress.

The colorimetric parameters show a heavy variation; xy shows an initial blue shift, then a yellow shift. This behavior can be better understood by looking at the PSD curves in Fig. 4, which are normalized with respect to the blue peak at 438 nm. As can be observed, the sample stressed at 2 A has no variation in the spectral shape, whereas the samples stressed at higher currents have a strong variation in the yellow range, with a first decrease of the yellow component and then an increase, that is compatible with the variation of the xy coordinates.

The main outcome of the stress is the heavy decrease in the optical emission, as observed in Fig. 3. This lowering is mainly due to the darkening of the area above the LED chips, as visible in the photos in Fig. 5(a), that show the devices at various stages of the stress. LEDs L1 does not show any degradation, whereas the other LEDs exhibit a strong darkening of the surface, whose kinetics are accelerated by the stress current: the higher the stress current, the earlier the darkening develops. In Fig. 5(b-c) are shown two close-ups of one stressed LED and of one LED with the lens removed. The stressed LED with the lens in place exhibits a darkening just above the LED chip, and also some lens

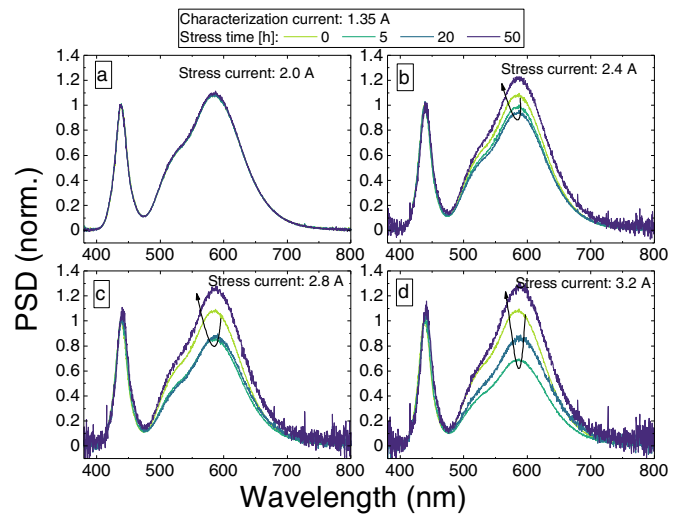


Fig. 4. Power spectral densities measured at 1.35 A, normalized at 438 nm, of L2 (a), L3 (b), L5 (c) and L7 (d) stressed at 2.0 A, 2.4 A, 2.8 A and 3.2 A, respectively.

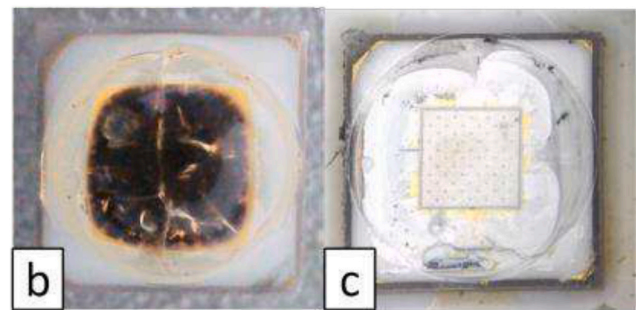
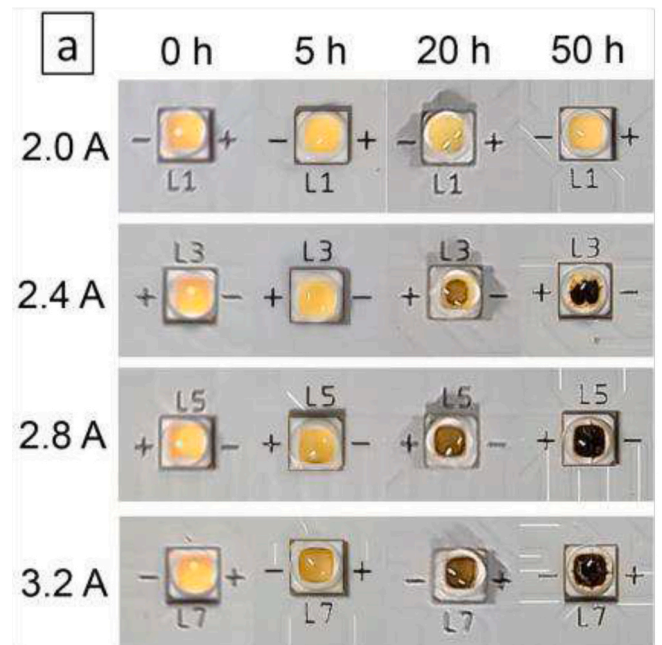


Fig. 5. Optical images of the LEDs during the stress (a) and close up of L8, stressed at 3.2 A, with lens (b) and of L5, stressed at 2.8 A, with lens and phosphors removed.

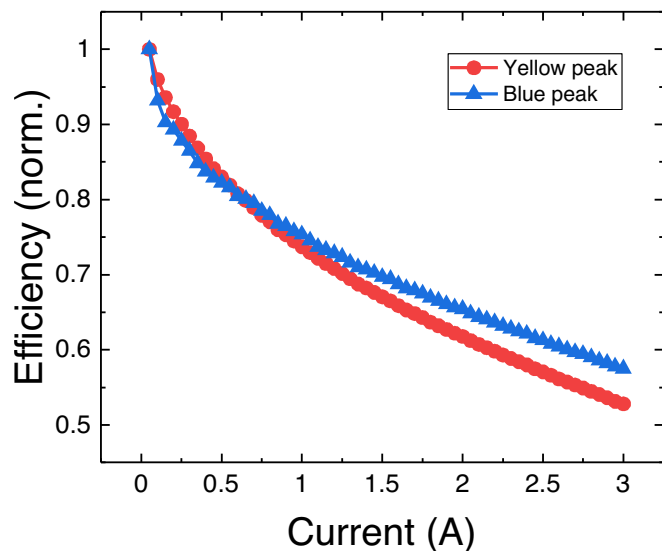


Fig. 6. Optical power conversion efficiency, normalized to the maximum value, for the blue peak (390–475 nm) and for the yellow region (475–750 nm) of an unstressed LED at 25 °C.

cracking, possibly due to thermomechanical stress. The device with the lens removed shows that the chip itself does not appear degraded, therefore the degradation must have originated in the phosphors and/or in the silicone lens.

It is interesting to analyze the optical power conversion efficiency, i. e. the ratio between the optical power and the electrical power, of the blue peak (390–475 nm region), related to the blue chip emission, and of the yellow peak (475–750 nm region), plotted in Fig. 6. It is possible to see that, with increasing current, both signals decrease, possibly due to increase in recombination losses [11]. However, yellow region efficiency decreases faster than blue peak efficiency.

To further investigate the root cause of the degradation, LEDs were removed from the PCB, and several cross-sections of the structures were made. The devices were encapsulated with epoxy resin and ground along one of their axes. The cross sections are shown in Fig. 7 where L2 (stressed at 2 A) and L5 (stressed at 2.8 A) are shown. The LED stressed at 2 A does not show any degradation at it is visible the chip itself, the phosphors layer and the lens, which adhere one on top of the other. On the other hand, the LED stressed at 2.8 A shows many interesting features: the darkening of the device mainly happens on the bottom part of the silicone lens, that is closer to the device die and, therefore, hotter. The phosphor layer looks slightly degraded, with some darker regions, but less than the silicone lens. Silicone cracking and a delamination of the phosphors layer from the chip itself are clearly visible. There is also evidence of cracking on the white insulating material on the side of the chip.

Therefore, these results support the thesis of combined chemical modification of the silicone material and thermo-mechanical cracking of

the lens [12,13]. These mechanisms are both accelerated by temperature and optical flux. Junction temperature is higher at higher currents; moreover, a higher optical flux increases thermal losses in the phosphor layers, since phosphor conversion efficiency drops at very high intensities, as noted in Fig. 1(b) and Fig. 6 [14]. Then, a thermal runaway process leads to extremely high temperatures in the region near the phosphors [15], eventually generating a darkening of the material [16–18].

#### 4. Raman analysis

An additional set of samples was submitted to an additional 50 h stress at currents ranging from 2.0 A (i.e. the absolute maximum rating) to 2.6 A (i.e. 1.3 times the absolute maximum rating) in 0.2 A steps to observe the repeatability of the previous experiment and the effect of the stress in samples at currents above to the absolute maximum, but very close to this value. The samples were then analyzed by means of photoluminescence and Raman spectroscopy using a 785 nm laser by Sol instruments and a MS750 series Monochromator-spectrograph at room temperature. The measurements taken on these samples were compared with the same measurements performed on an unstressed sample. The measurements were made by focusing the laser on the top of the sample (i.e. near the surface of the lens) by using two different objective lenses, 10× and 50×, which have different penetration depths: the former penetrates in the first 5 μm of the silicone lens, the latter stops in the first 0.5 μm.

In Fig. 8 (a) the photoluminescence spectra of the samples, acquired with the 50× lens, is plotted. It is possible to note that the unstressed sample and the sample stressed at the lowest current (2 A) do not exhibit any luminescence (both curves are superimposed and have no signal), whereas the samples stressed at higher currents have a strong luminescence band, whose intensity is proportional to the stress current.

Raman spectra are shown in Fig. 8(b). In the unstressed sample and in the sample stressed at 2 A there are some peaks clearly visible (at 620  $\text{cm}^{-1}$ , 1000  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$ ), which are still present in the stressed samples, superimposed to the luminescence band. These peaks were observed in other samples with silicone [19]. Usually, LEDs feature silicone lenses made of polydimethylsiloxane, polyphenylsiloxane or poly(*methyl,phenyl*)siloxane [3]. In this case, we are possibly in the second or third case, since the peaks at around 1000  $\text{cm}^{-1}$  and 1030  $\text{cm}^{-1}$  are fingerprints of the phenyl group [20]. Polysiloxanes with phenyl side group exhibit higher decomposition temperatures with respect to polydimethylsiloxanes, and begins to decompose at temperatures higher than 150 °C, with the breaking of Si–O bonds and the formations of cyclic oligomers and, at higher temperature, the breaking of Si-phenyl bonds [21,22]. At very high temperature and high heating rate a thermal oxidative degradation can be observed in silicones, with the formation of a fine powder that could be the cause of silicone degradation observed in LEDs stressed at the highest current and, therefore, reaching higher silicone temperatures [23].

It is possible to see that unstressed sample and the sample stressed at the lowest current, that does not show significant optical power

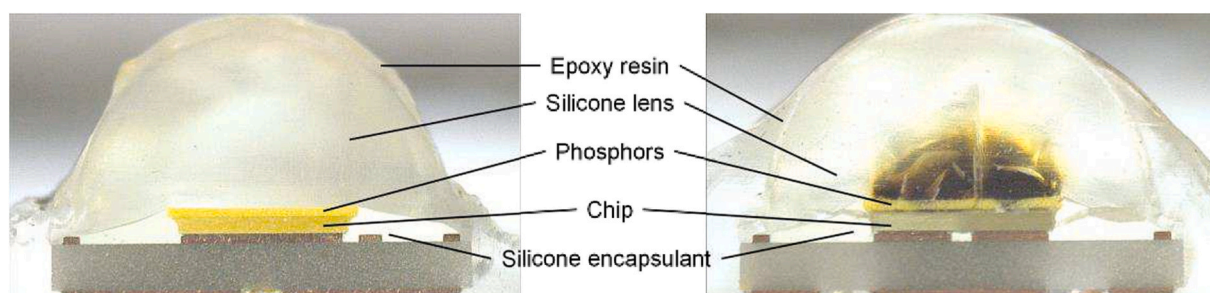


Fig. 7. Mechanical cross-section of device L2 (left), stressed at 2 A, and of device L5 (right), stressed at 2.8 A.

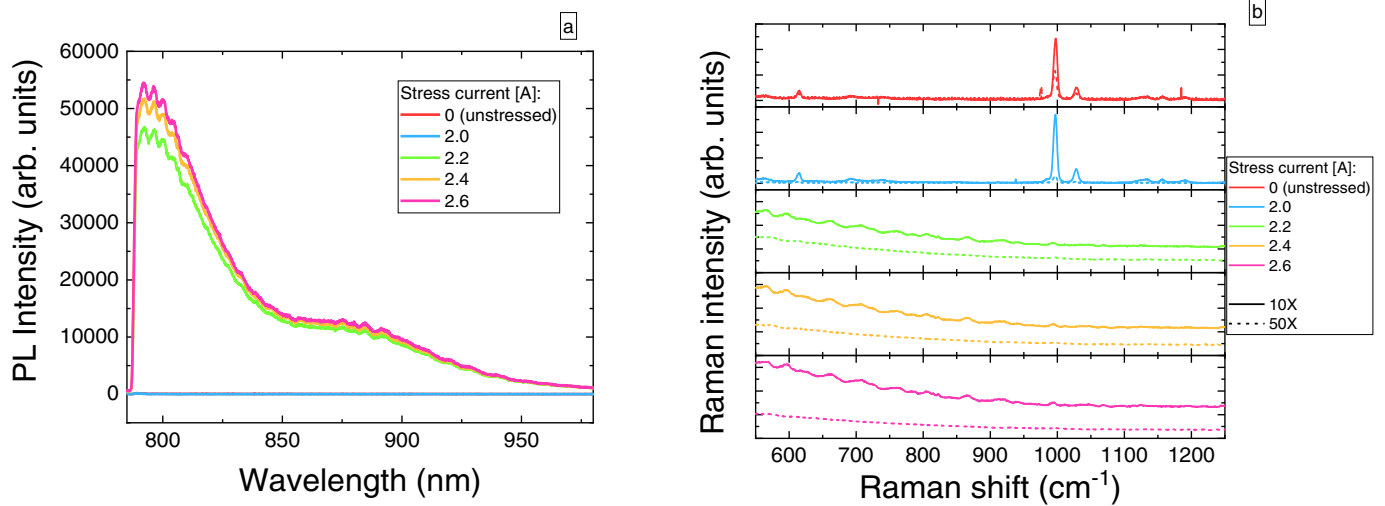


Fig. 8. Photoluminescence spectra (a) and Raman spectra (b) of the unstressed and stressed samples under 785 nm laser excitation.

degradation, have very similar Raman spectra with slight variations in signal strengths. In the samples stressed at currents of 2.2 A and higher, Raman peaks remain barely visible, but the luminescence is stronger in these samples. Therefore, this supports the hypothesis of a process of degradation of the silicone lens, that goes from the inside of the device to the outside, which has a certain temperature that is reached by the devices stressed at the highest temperatures.

## 5. Conclusions

In this work, we analyzed the robustness of high power white LEDs and their degradation induced by electrical stress with currents above the limits specified by the manufacturer. We found a slight increase in leakage current, proportional to stress current, possibly due to an increase in the density of defects in the active region of the devices. The LEDs stressed above the absolute maximum rating showed a strong optical power decrease in just 50 h of stress and a visible darkening of the area above the chip. By cross-sectioning the devices, we observed a delamination of the phosphors from the chip surface and a heavy darkening of the lens just above the chip. Photoluminescence and Raman spectroscopy showed an increase in luminescence in the degraded samples. We hypothesized that stress at very high current levels caused a thermal runaway process, promoted by the combined action of the high temperatures reached by the devices and of the drop in efficiency reached by the phosphors submitted to high optical powers. This eventually led to the degradation and darkening of the lens, causing an almost catastrophic failure of the devices.

This indicates the importance of using a silicone that is stable at high temperature when designing the device package. Moreover, the extreme sensitivity of the failure process to the stress current must be taken into account in the design of a proper thermal management system, that also account for phosphors-generated heat, when building a solid-state lighting system.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## Acknowledgements

This work has received funding from the ECSEL Joint Undertaking (ECSEL-JU) under grant agreement No 101007319. The JU receives support from the European Union's Horizon 2020 research and innovation programme and Netherlands, Hungary, France, Poland, Austria, Germany, Italy, Switzerland. The presented results are reflecting only the author's view: ECSEL-JU is not responsible for any use that may be made of the information it contains.

## Author statement

All authors contributed equally to this paper.

## References

- [1] Grand View Research, LED lighting market size, share & trends analysis report by product (lamps, luminaires), by application (indoor, outdoor), by end-use (commercial, residential, industrial), by region, and segment forecasts, 2023–2030. <https://www.grandviewresearch.com/industry-analysis/led-lighting-market>.
- [2] N. Trivellini, M. Meneghini, M. Buffolo, G. Meneghesso, E. Zanoni, Failures of LEDs in real-world applications: a review, *IEEE Trans. Device Mater. Reliab.* 18 (2018) 391, <https://doi.org/10.1109/TDMR.2018.2852000>.
- [3] M. Yazdan Mehr, A. Bahrami, W.D. van Driel, X.J. Fan, J.L. Davis, G.Q. Zhang, Degradation of optical materials in solid-state lighting systems, *Int. Mater. Rev.* 65 (2020) 102, <https://doi.org/10.1080/09506608.2019.1565716>.
- [4] W.D. van Driel, X.J. Fan (Eds.), *Solid State Lighting Reliability* Springer New York, New York, NY, 2013.
- [5] W.D. van Driel, X. Fan, G.Q. Zhang (Eds.), *Solid State Lighting Reliability Part 2*, Springer International Publishing, Cham, 2018.
- [6] A. Rogers, The great purpling. *Business insider*. <https://www.businessinsider.com/led-city-streetlights-turning-purple-broken-tech-danger-2022-11>.
- [7] Y. Xi, E.F. Schubert, Junction-temperature measurement in GaN ultraviolet light-emitting diodes using diode forward voltage method, *Appl. Phys. Lett.* 85 (2004) 2163, <https://doi.org/10.1063/1.1795351>.
- [8] M. Mandurino, G. Verzellesi, M. Goano, M. Vallone, F. Bertazzi, G. Ghione, M. Meneghini, G. Meneghesso, E. Zanoni, Physics-based modeling and experimental implications of trap-assisted tunneling in InGaN/GaN light-emitting diodes, *Phys. Status Solidi* 212 (2015) 947, <https://doi.org/10.1002/pssa.201431743>.
- [9] M. Auf der Maur, B. Galler, I. Pietzonka, M. Strassburg, H. Lugauer, A. Di Carlo, Trap-assisted tunneling in InGaN/GaN single-quantum-well light-emitting diodes, *Appl. Phys. Lett.* 105 (2014), 133504, <https://doi.org/10.1063/1.4896970>.
- [10] M. Musolino, D. van Treeck, A. Tahraoui, L. Scarparo, C. De Santi, M. Meneghini, E. Zanoni, L. Geelhaar, H. Riechert, A physical model for the reverse leakage current in (In,Ga)N/GaN light-emitting diodes based on nanowires, *J. Appl. Phys.* 119 (2016) 44502, <https://doi.org/10.1063/1.4940949>.
- [11] M. Meneghini, C. De Santi, A. Tibaldi, M. Vallone, F. Bertazzi, G. Meneghesso, E. Zanoni, M. Goano, Thermal droop in III-nitride based light-emitting diodes: physical origin and perspectives, *J. Appl. Phys.* 127 (2020), 211102, <https://doi.org/10.1063/5.0005874>.

- [12] M.-H. Chang, D. Das, P.V. Varde, M. Pecht, Light emitting diodes reliability review, *Microelectron. Reliab.* 52 (2012) 762, <https://doi.org/10.1016/j.microrel.2011.07.063>.
- [13] H. Xu, Y. Tang, J. Wu, B. Peng, Z. Chen, Z. Liu, The Study on Cracking Reasons of LED Encapsulation Silicone. 2019 20th Int. Conf. Electron. Packag. Technol., IEEE, 2019, p. 1, <https://doi.org/10.1109/ICEPT47577.2019.2452888>.
- [14] R.-J. Xie, N. Hirotsaki, N. Kimura, K. Sakuma, M. Mitomo, 2-phosphor-converted white light-emitting diodes using oxynitride/nitride phosphors, *Appl. Phys. Lett.* 90 (2007), 191101, <https://doi.org/10.1063/1.2737375>.
- [15] X. Luo, X. Fu, F. Chen, H. Zheng, Phosphor self-heating in phosphor converted light emitting diode packaging, *Int. J. Heat Mass Transf.* 58 (2013) 276, <https://doi.org/10.1016/j.ijheatmasstransfer.2012.11.056>.
- [16] P. McCluskey, K. Mensah, C. O'Connor, A. Gallo, Reliable use of commercial technology in high temperature environments, *Microelectron. Reliab.* 40 (2000) 1671, [https://doi.org/10.1016/S0026-2714\(00\)00188-8](https://doi.org/10.1016/S0026-2714(00)00188-8).
- [17] P. McCluskey, K. Mensah, C. O'Connor, F. Lillie, A. Gallo, and J. Fink, Reliability of commercial plastic encapsulated microelectronics at temperatures from 125°C to 300°C. 2000 IEEE Aersp. Conf. Proc. (Cat. No.00TH8484), IEEE, n.d., p. 445, DOI: <https://doi.org/10.1109/AERO.2000.878520>.
- [18] Longzao Zhou, Bing An, Wu Yiping, Shunhong Liu, Analysis of delamination and darkening in high power LED packaging, in: 2009 16th IEEE Int. Symp. Phys. Fail. Anal. Integr. Circuits, IEEE, 2009, p. 656, <https://doi.org/10.1109/IPFA.2009.5232549>.
- [19] J. Kim, B. Ma, K. Lee, Study on influence of silicone encapsulant for ceramic LED package after HTOL test, in: Proc. 5th Electron. Syst. Technol. Conf., IEEE, 2014, p. 1, <https://doi.org/10.1109/ESTC.2014.6962856>.
- [20] A.W. Salamon, K.J. Fielder, Infrared and Raman analysis of polymers, *Handb. Plast. Anal.* 198 (2003), <https://doi.org/10.1201/9780203911983-12>.
- [21] W. Zhou, H. Yang, X. Guo, J. Lu, Thermal degradation behaviors of some branched and linear polysiloxanes, *Polym. Degrad. Stab.* 91 (2006) 1471, <https://doi.org/10.1016/j.polymdegradstab.2005.10.005>.
- [22] M. Narisawa, Silicone resin applications for ceramic precursors and composites, *Materials (Basel)*. 3 (2010) 3518, <https://doi.org/10.3390/ma3063518>.
- [23] G. Camino, S. Lomakin, M. Lazzari, Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects, *Polymer (Guildf)*. 42 (2001) 2395, [https://doi.org/10.1016/S0032-3861\(00\)00652-2](https://doi.org/10.1016/S0032-3861(00)00652-2).